



United States Department of the Interior

U.S. GEOLOGICAL SURVEY
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**NATIONAL WATER QUALITY LABORATORY
TECHNICAL MEMORANDUM 2013.01**

20 November 2013

Subject: Procedure used to correct axial-view lithium results determined by inductively coupled plasma – optical emission spectrometry (ICP-OES)

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PURPOSE

A procedure to correct axial-view lithium concentrations derived from inductively coupled plasma – optical emission spectrometry (ICP-OES) for bias associated with ionization interference has been validated and applied to affected data from 1 March 2012 through 31 October 2013 to correct results determined by the U.S. Geological Survey (USGS) National Water Quality Laboratory (NWQL).

The purposes of this technical memorandum are to describe the procedure used to correct lithium data and illustrate the accuracy of the correction equation.

BACKGROUND

Dissolved and whole-water recoverable lithium were determined using radial-view ICP-OES prior to 2003. With the implementation of updated instrumentation, lithium has been measured since 2003 using axial-view ICP-OES to improve the reporting level. Validation studies at the time indicated that there was no significant difference between results obtained using the axial- and radial-views for the samples having a wide range of dissolved solids concentrations.

Approximately in March 2012, however, some lithium data for USGS Branch of Quality Systems Inorganic Blind Sample Program's samples were positively biased. Investigation determined that the probable root cause for the shift in data quality was ionization interference likely caused when lithium was removed from a calibration standard containing high concentrations of alkali and alkali earth elements in March 2012; no bias in lithium results was indicated prior to March 2012.

Ionization interference occurs in samples having relatively high concentrations of alkali (that is, sodium and potassium) and/or alkali earth elements (that is, calcium and magnesium). Axial-view lithium determinations were discontinued after 31 October 2013 and radial-view lithium determinations were implemented since ionization interference is substantially reduced when using the radial-view—regardless of the chemical makeup of the calibration solution.

The shorter path length in the radial-view affects the method detection level. The reporting levels for lithium in dissolved and whole-water samples analyzed using axial-view were 0.05 and 0.04 µg/L, respectively, whereas the interim method detection limits are 0.1 and 0.4 µg/L, respectively, when using the radial-view.

RESULTS

Correcting for bias. A procedure to correct axial-view lithium concentrations for bias associated with ionization interference was established by modeling the axial and radial lithium results relative to alkali and alkali earth concentrations for over 100 dissolved and whole-water samples submitted to NWQL during fiscal years 2012–13. Samples from across the United States as well as eight from the Branch of Quality Systems Inorganic Blind Sample Program were used. The lithium concentrations in the model samples ranged from 0.2 to over 4,000 µg/L, whereas the total concentration of calcium (Ca), magnesium (Mg), sodium (Na), and potassium (K) ranged from 10 to over 20,000 mg/L.

Linear least squares regression of the ratio of the axial-lithium concentration to the radial-lithium concentration as a function of \log_{10} (Ca+Mg+Na+K) concentration, as shown in fig. 1, resulted in an equation that can be used to convert axial-lithium results to radial-lithium results if Ca, Mg, Na, and K concentrations are known. The regression equation is

$$(\text{axial-Li} / \text{radial-Li}) \text{ ratio} = 0.3062 \times \log_{10} (\text{Ca+Mg+Na+K, in mg/L}) + 0.7748 \quad (1)$$

After determining the (axial-Li / radial-Li) ratio for a particular sample from equation 1, the radial-Li concentration is calculated by dividing the previously measured axial-Li concentration by the (axial-Li / radial-Li) ratio.

Accuracy of the correction equation. Graphs show the accuracy of the correction equation for another group of dissolved ($n = 526$; fig. 2) and whole-water samples ($n = 420$; fig. 3) collected during fiscal years 2012–13. Results for lithium from measured radial-ICP-OES are compared to calculated radial-lithium results from equation (1).

For the dissolved samples tested, there is approximately a 6 percent positive bias between the measured and calculated radial-lithium concentrations; for whole-water samples, there is about a 6 percent negative bias. This bias signifies the overall accuracy of the correction for the range of lithium, alkali, and alkali earth concentrations in the samples used in the evaluation. Perfect correlation between the measured and calculated results would give a regression line with a slope equal to 1.0.

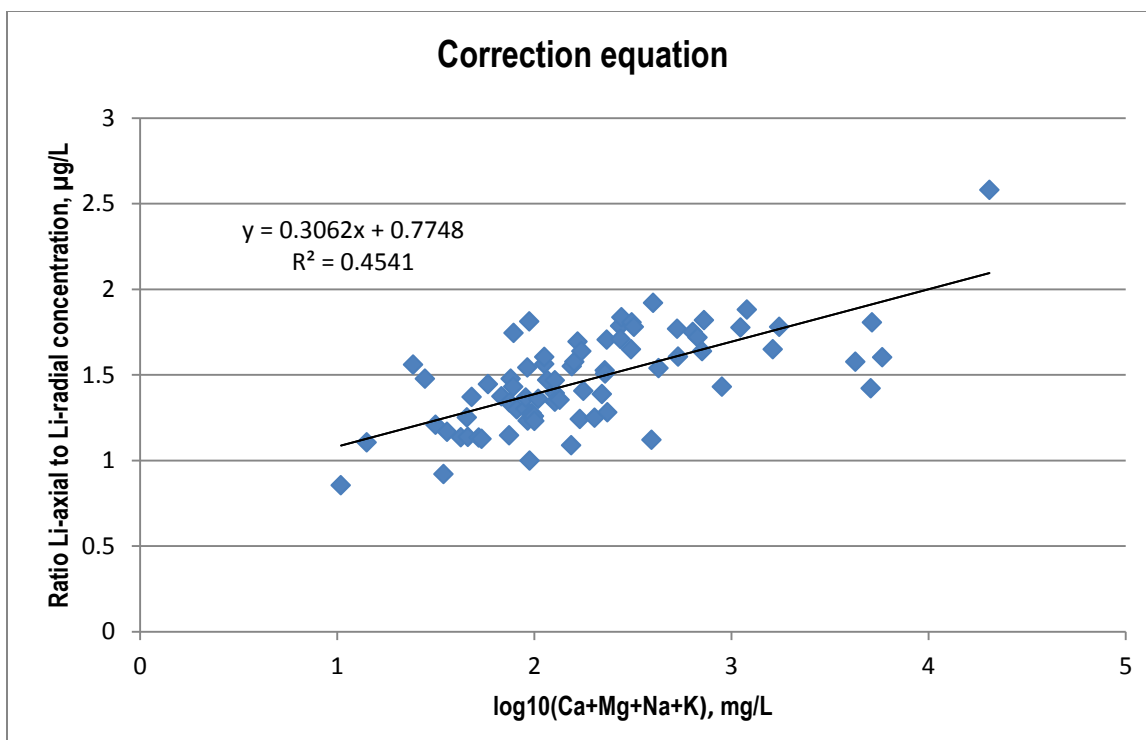


Figure 1. Bias correction equation derived from the lithium concentration measured in both the axial and radial modes for 100 model water samples as a function of the \log_{10} calcium, magnesium, sodium, and potassium concentrations.

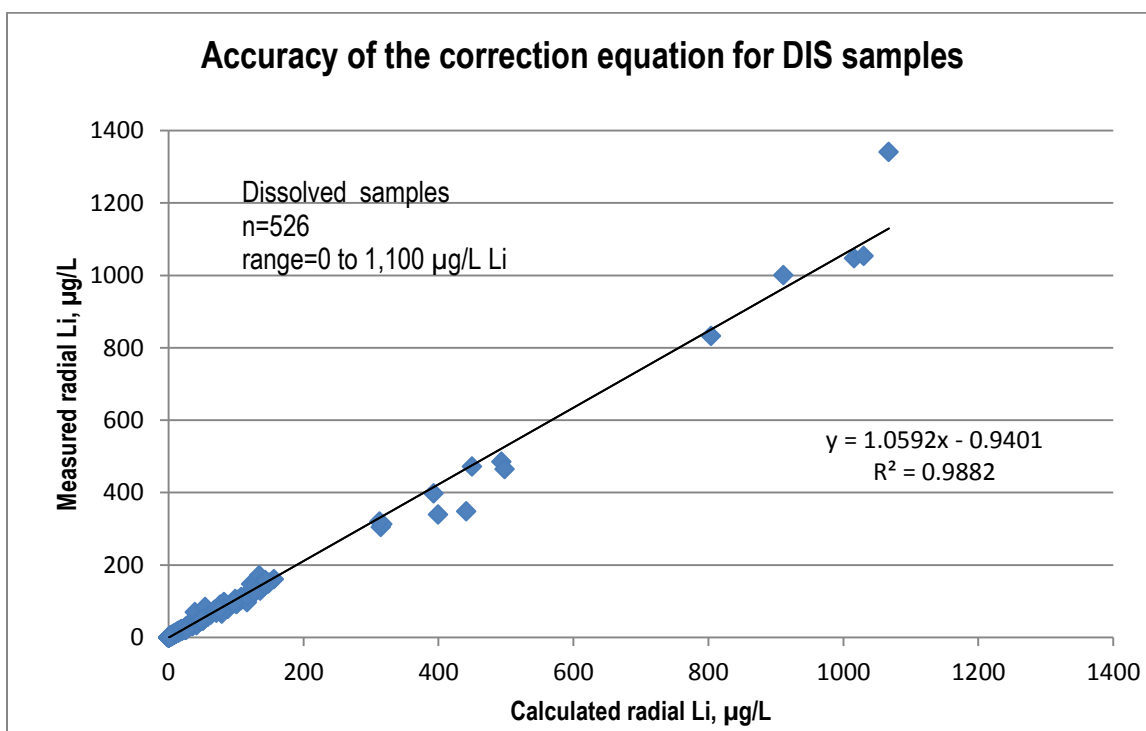


Figure 2. Accuracy of the correction equation for dissolved water samples (DIS).

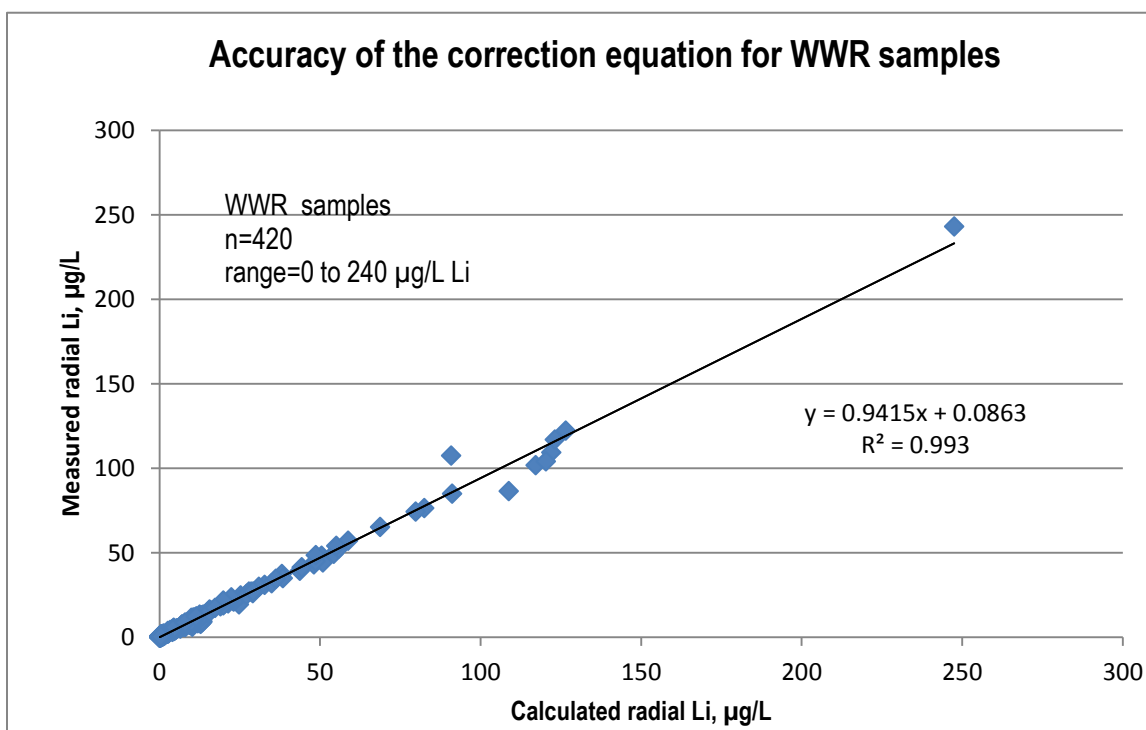


Figure 3. Accuracy of the correction equation for whole-water samples (WWR).

Effect on database: limited to update of affected data

/signed/
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